MARS ATMOSPHERIC ESCAPE RECORDED BY H, C AND O ISOTOPE RATIOS IN CARBON DIOXIDE AND WATER MEASURED BY THE SAM TUNABLE LASER SPECTROMETER ON THE CURIOSITY ROVER. C. R. Webster[1], P. R. Mahaffy[2], L. A. Leshin[3], S. K. Atreya[4], G. J. Flesch[1], J. Stern[2], L. E. Christensen[1], A. R. Vasavada[1], T. Owen[5], P. B. Niles[6], J. H. Jones[7], H. Franz[2], and the MSL Science Team, [1] Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., Pasadena, CA 91109, Chris.R.Webster@jpl.nasa.gov [2]NASA Goddard Space Flight Center (GSFC), Greenbelt, MD 20771, [3]Rensselaer Polytechnic Institute, Troy, NY 12180, [4]University of Michigan, MI 48105, [5]University of Hawaii, Honolulu, HI 96822, [6]NASA Johnson Space Center, Houston, TX 77058, [7]University of Arizona, Tucson, AZ 85721.

Summary: In situ measurements of the isotopic ratios of D/H in water, and $^{13}C/^{12}C$, $^{18}O/^{16}O$, $^{17}O/^{16}O$ and $^{13}C^{18}O/^{12}C^{16}O$ in carbon dioxide have been made in the Martian atmosphere. As part of the Sample Analysis at Mars (SAM) suite [1] on the Curiosity Rover, the tunable laser spectrometer (TLS) has achieved unprecedented precision for a planetary measurement of these isotopic ratios that record escape of lighter gases from the early Mars atmosphere and subsequent surface interactions.

Introduction: Stable isotope ratios in C, H, N, O and S are powerful indicators of a wide variety of planetary geophysical processes that can identify origin, transport, temperature history, radiation exposure, atmospheric escape, environmental habitability and biological activity [2]. For Mars, measurements to date have indicated enrichment in all the heavier isotopes consistent with atmospheric escape processes, but with uncertainty too high to tie the results with the more precise isotopic ratios achieved from SNC meteoritic analyses.

We will present results to date of H, C and O isotope ratios in CO_2 and H_2O made to high precision (few per mil) using the Tunable Laser Spectrometer (TLS) that is part of the Sample Analysis at Mars (SAM) instrument suite on MSL's Curiosity Rover.

Measurement Method: TLS is a two-channel tunable laser spectrometer that uses direct and second harmonic detection of IR laser light absorbed after multi-passing a sample cell [3]. One laser source is a near-IR tunable diode laser at 2.78 µm that can scan two spectral regions containing CO_2 and H_2O isotopic lines; the second laser source is an interband cascade laser at 3.27 µm used for methane detection alone (not reported here). For the results reported here, the near-IR laser makes 43 passes of a 20-cm long Herriott cell that is evacuated using a turbomolecular pump for background scans, then filled to 0.74 mbar using volume expansion of Mars air typically at 7 mbar. During data collection, the Herriott cell and other optics are kept at 47±3 ^{o}C using a ramped heater that spoils any interference fringes during the 2-minute sample period.

The background amounts of both CO_2 and H_2O are negligible and also reflect insignificant contribution to the signal from the instrument foreoptics. The laser scans every second through the spectral regions. Each spectrum is co-added on board to downlink 2-minute spectra for a given run, typically ~30 mins. Spectra are collected for several ~30-minute runs on six days (Martian Sols 28, 53, 73, 79, 81, & 106).

Spectral regions. TLS scans over individual rovibrational lines in two spectral regions near 2.78 µm; one centered at 3590 cm^{-1} for CO_2 isotopes, and a second centered at 3594 cm^{-1} for both CO_2 and H_2O isotopes. The lines used in both regions have no significant interferences. In the 3594-cm^{-1} region, CO_2 and H_2O lines used interleave across the spectrum without interference, allowing accurate isotope ratios across widely-varying CO_2 and H_2O abundances in both atmospheric and evolved gas experiments.

Isotope Ratio Determination. After normalization to the laser power and zero light pulse, spectral lines are processed individually by integrating over the line shape; line ratios are then related to those expected from calibration runs, using the HITRAN parameters if necessary to adjust for minor temperature differences. Calibration of the relative absorptions of isotopic pair lines was done pre-launch using certified isotopic gas mixtures (Oztech) and Boulder water independently certified by NOAA. Although spectral SNR's are typically a few thousand, the data show scatter larger than this, and the reported results for any single run (Sol) are a mean value and 2-stderr on the results.

Results for CO_2 isotopes: The preliminary mean isotopic ratios from the six atmospheric runs and the 2-stderr uncertainty are given in Table 1. Values are given relative toVPDB for $d^{13}C$ and relative to VSMOW for all oxygen isotopes. Independent SAM TLS and QMS results for d13C agree well, but disagree with the much lower Phoenix lander result [4].

Results for H_2O isotopes: For atmospheric runs, measured water abundances of up to 1% by volume in our Herriott cell exceed those expected (~150 ppmv) in Martian air. Since our measured dD values (Table 2)

are clearly Martian and not terrestrial, we attribute the high water mixing ratios to either high near-surface humidity (natural or from enhanced temperatures in the vicinity of the rover) or to water entrained from frozen or liquid sources on or near the heated inlet valves. The relatively high water amounts give good SNR in our HDO, $H_2^{18}O$ and $H_2^{16}O$ lines. Also, in evolved gas experiments from pyrolysis of solid surface samples, we see water coming off at relatively low temperatures (<120°C) that we attribute to adsorbed water whose D/H ratio is also representative of the Martian atmosphere. Detailed results to date for delta-D and delta-^{18}O in water will be presented.

References:

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Table 1. Carbon Dioxide Isotope Ratios ‰ ± 2stderr

Measurement	delta-13C	delta-18O
SAM-TLS	**45±4**	**48±6**
SAM-QMS	40±11	N/A
Phoenix Lander [4]	-2.5±4.3	31±5.7
Viking NMS [5]	23±43	7±44
SNC meteorites [6]	36±10	3.9-5.4 ±0.1

Table 2. Water Isotope Ratios ‰ ± 2stderr

Measurement	delta-D	delta-18O
SAM-TLS	**5,000-7,000**	**50±10**
Earth telescopes [7]	2,000 –9,000	N/A

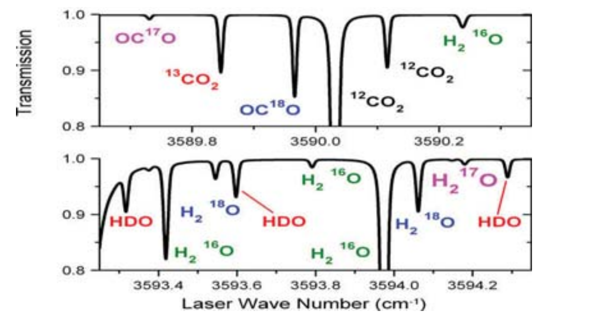

Fig. 1. Spectral scan regions used by MSL-SAM's TLS instrument for measuring CO_2 and H_2O isotope ratios.

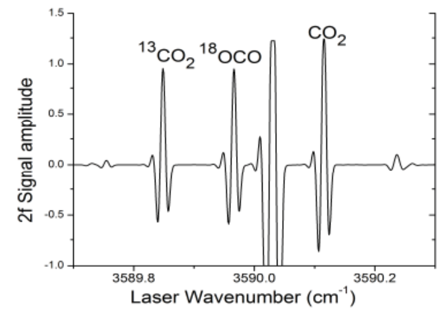

Figure 2. Example of single two-minute spectrum downloaded from Curiosity. Noise levels are less than 1/1000th of the prinicipal isotope lines ratioed. Isotope ratios for water and carbon dioxide are also recorded in a second wavelength region (see text).

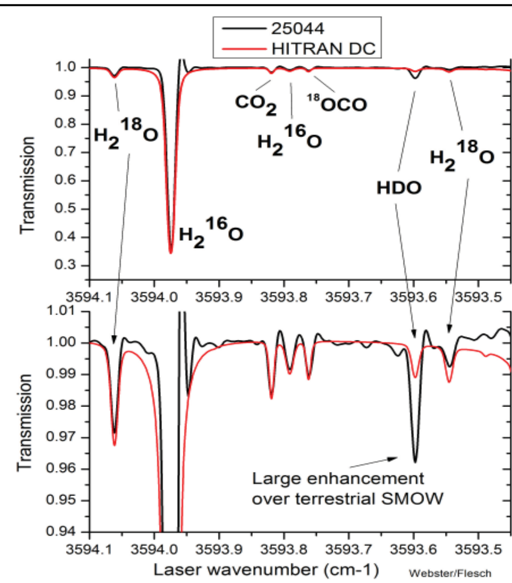

Figure 3. Middle section of a single region 2 spectrum downloaded from Curiosity, showing observed large HDO line depth compared to calculated HITRAN spectrum based on terrestrial water isotope ratios.